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To cite this article: A V Suzdaltsev *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **918** 012108

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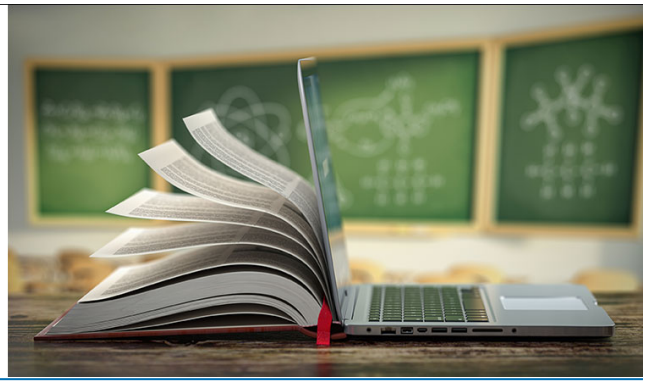

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IOP Conf. Series: Materials Science and Engineering **918** (2020) 012108 doi:10.1088/1757-899X/918/1/012108

Monitoring alumina content in cryolite-alumina melt

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Abstract. Alumina content in electrolysis cells for aluminum production is one of the most important and poorly controlled parameters. The alumina is delivered to the cell by means of an alumina automatic feeding system, adjusted to the amperage or to the voltage alteration. However, a change in the alumina content in the cryolite-alumina melt depends not only on the current; and the voltage is not a parameter that responds only to the alumina amount in the melt. In order to check the current value of alumina content as well as the dissolution of alumina in industrial electrolytes (NaF-AlF_3-CaF_2-Al_2O_3), a novel electrochemical sensor was proposed. It was comprised of a carbon working electrode and a counter electrode interacting with aluminum. The sensor was easy to manufacture, and it allowed reducing the measurement error associated with back reactions at the working electrode. The novel approach was considered on an ex-ample of dissolving the alumina in the NaF-AlF_3-(5 wt%)CaF_2 melt ([NaF]/[AlF_3] = 2.1 mol/mol) containing alumina (Al_2O_3) in amount of 0.69-4.51 wt% at 970 °C in conditions of natural and forced convection. It was found that the alumina solubility in the studied melt was 4.51 wt%. Depending on the initial content of alumina in the melt and convection conditions, its dissolution rate varied up to 0.36 mol/s·m^3.

1. Introduction

The existing electrolytic production of aluminum is one of the most inefficient technologies in the metallurgical industry due to the fact that most of the energy expended is scattered into the environment [1-3]. For this reason, existing technologies are optimized and novel techniques and electrolyzers with a reduced specific energy consumption per ton of aluminum are developed [4-10].

One of the ways to improve the performance of aluminum production is to optimize the alumina feeding into the electrolytic cells, since such parameters as voltage, cathodic efficient, and anode consumption depend on the alumina content in the cryolite-alumina melt. It is recommended [1-3] to maintain the alumina content in the range of 1.5-3.0 wt% in the NaF-AlF_3-CaF_2-Al_2O_3 conventional electrolytes in order to increase the efficiency and service life of the electrolyzer. Currently, this is provided by the automatic alumina feeding system, adjusted to the values of current or voltage in the cell. However, a change in the alumina content in the cryolite-alumina melt depends not only on the current value, and the voltage is not a parameter that responds only to the alumina content in the melt.

According to the analysis of the scientific and technical data sources it follows that the most accurate and efficient alumina content in the cryolite-alumina melt can be determined by two independent methods:

- analysis of electrolyte samples, taken from the bath, by physicochemical techniques in the analytical lab of enterprise;
- measurement directly in the bath of the property or parameter of the investigated system, which reliably and reasonably correlating with the content of alumina dissolved in the melt [11-15].

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The alumina content monitoring methods directly in the bath are poorly developed, and the analytical control methods used in industrial laboratories are based on carbothermic reduction. The disadvantages of the latter are the delay in the results and the error associated with the possible ingress of undissolved alumina into the sample.

The most studied is the electrochemical approach for monitoring the alumina content, including measuring peak value of the current response dependence on an immersed graphite anode during its fast polarization. The peak current values in a certain range correlate with the concentration of electroactive particles and alumina in the melt.

In the present work, preliminary tests were carried out using an electrochemical sensor of a new optimized design with the purpose of determining the fundamental possibility of studying a process of alumina dissolution, as well as monitoring the current content of alumina in a cryolite-alumina melt of industrial composition.

The data obtained are necessary to optimize a complex math model of conjugate physical fields (electric, electromagnetic, temperature) by describing considerations regarding the dissolution and distribution of alumina in the electrolyzer.

2. Experiment

New electrochemical sensor (device) consisting of a carbon working electrode and a counter electrode made of copper or another metal interacting with aluminum was proposed (Figure 1). The sensor was completed as follows: a working inclined electrode was shielded by an insulator of boron nitride up to 1 mm thick and placed in a corundum tube, from the other end of which a current lead was connected to the working electrode. The counter electrode, made in the shape of a copper ring with a surface several times larger than the surface of the working electrode, was attached to the corundum tube outside.
The application of such design makes it possible to exclude the influence of dissolved aluminum due to the greater (in comparison with the known devices) distance between the working and the counter electrodes and the interaction of aluminum with the material of the counter electrode.

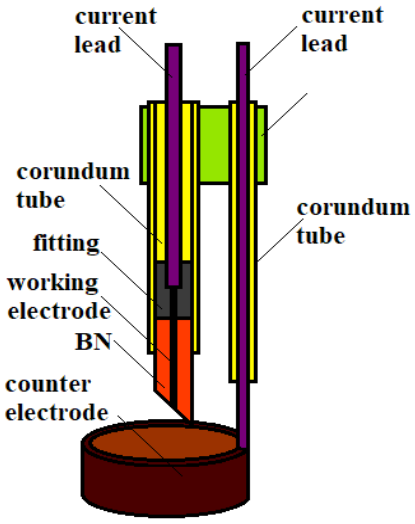

Figure 1. Electrochemical sensor of oxygen in cryolite-alumina melt.

The melts were prepared from individual fluorides NaF, AlF_3, and CaF_2 (Reakhim, Russia) according to the previously described procedure [16]. During measurements the alumina (Al_2O_3) (Reakhim, Russia) was added to the melts. The melts composition was determined by an inductively coupled plasma spectral-emission method and the X-ray phase analysis using an iCAP 6300 Duo spectrometer (Thermo scientific, USA) and a Rigaku D / MAX-2200VL / PC diffractometer (Rigaku, Japan).

The alumina dissolution process in the NaF-AlF_3-(5wt%)CaF_2 melt with a molar ratio of $[NaF]/[AlF_3]$ = 2.1 mol/mol at 970 °C and an alumina (Al_2O_3) content from 0.69 to 4.51 wt% was studied in conditions of natural and forced convection. Lab electrolyzer with a current of 20 A and amount of melt up to 1 kg was manufactured for this purpose. The melt was situated in a graphite crucible placed

in a corundum container. Studying the dissolution process and monitoring current alumina content in the melt were carried out using an electrochemical sensor and PGSTAT AutoLab 302N and NOVA 1.12 software (MetrOhm, Netherlands); the current-voltage dependences were obtained at a speed of 1 V/s, from which the peak value of the current response was determined. At the same time, the melt samples were taken and the alumina content was determined by carbothermal reduction of melt samples with subsequent fixation of infrared absorption on a LECO OH 836 analyzer (LECO Corp., USA). An empirical dependence was obtained from the values of measured peak current response and the analytical values of the alumina content, which was used both to monitor the current alumina content in the melt and to study peculiarities of its dissolution.

3. Results and discussion

The voltammograms obtained using an electrochemical sensor in the NaF-AlF_3-CaF_2-Al_2O_3 melt depending on the alumina content at 970 °C are presented in Figure2. It can be seen that under the selected measurement conditions the peak values of the current response recorded by the sensor depend on the alumina content. Therefore, the sensor can be used for operational monitoring of alumina in the melt if an empirical dependence was previously obtained.

An example of the empirical dependence of the peak value of the current response on the alumina content in the melt, obtained according to the measurements results in melts with natural and forced convection, is given in Figure 3. It is clear that the readings are described with high reliability by a single linear dependence up to an alumina content of 4.51 wt%. This value is the alumina solubility in the melt under experimental conditions.

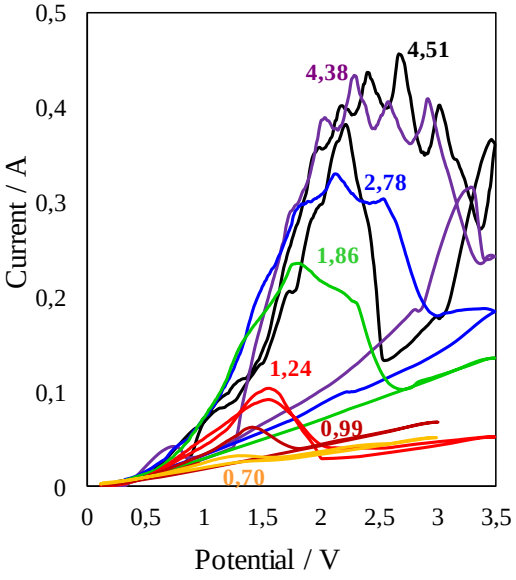

Figure 2. Voltammograms obtained in the NaF-AlF_3-(5 wt%)CaF_2-Al_2O_3 melt depending on the alumina content at 970 °C. The potential sweep speed is 1 V/s

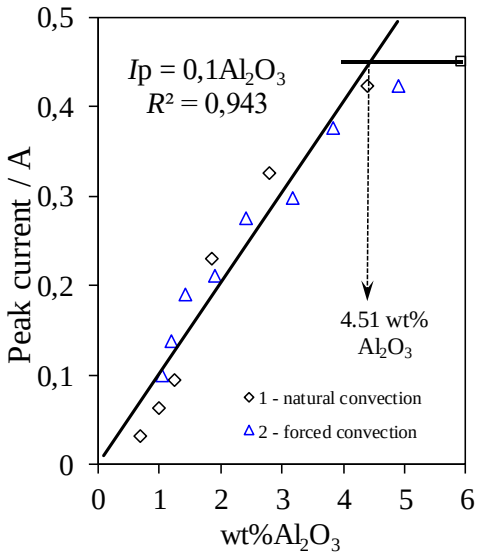

Figure 3. The dependence of the peak value of the current response on the alumina content in the NaF-AlF_3-CaF_2 melt ([NaF]/[AlF_3] = 2.1 mol/mol) at 970 °C

In order to study the peculiarities of the alumina dissolution the voltammograms were obtained using the electrochemical sensor depending on the contact time of the next alumina addition with the melt. The example of the peak value dependence of the cur-rent response on the dissolution time of the next alumina addition to the melt is shown in Figure4. It is revealed that when the alumina content is up to 3-3.5 wt%, its dissolution occurs intensively in 5-60 s, while the change in the peak value of the current response is described by a logarithmic dependence. A further increase in the alumina content in the melt drastically slows down the dissolution process.

Obtained empirical dependences of the change in the peak value for the current response were used in order to estimate the alumina dissolution rate. The values of the integral rate of complete dissolution

of alumina additions depending on the content of alumina in the melt and convection conditions are given in Figure5. Considering the initial alumina content, the integral rate is up to 0.36 mol/s·m^3. The obtained values are comparable with the rates of alumina dissolution in the cryolite-alumina melt, determined by the potentiometric and visual method [17–20]. The dynamic dissolution rate of the alumina additions at the initial moments of its contact with the melt reaches 6.9 mol/s·m^3.

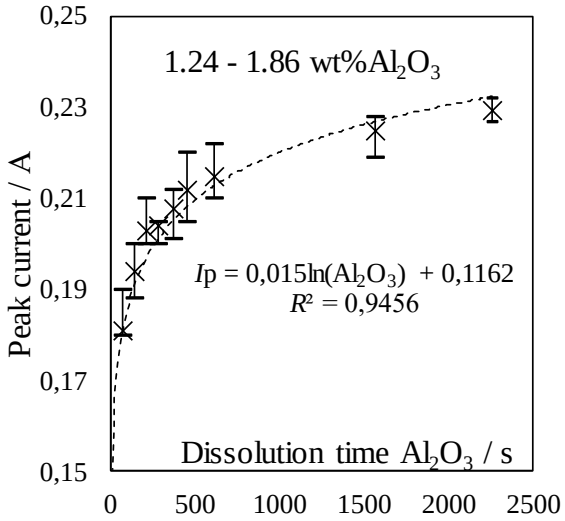

Figure 4. Change in the peak value of the anode current response with variation of the alumina content in the NaF-AlF_3-CaF_2 melt under natural convection at 970 °C.

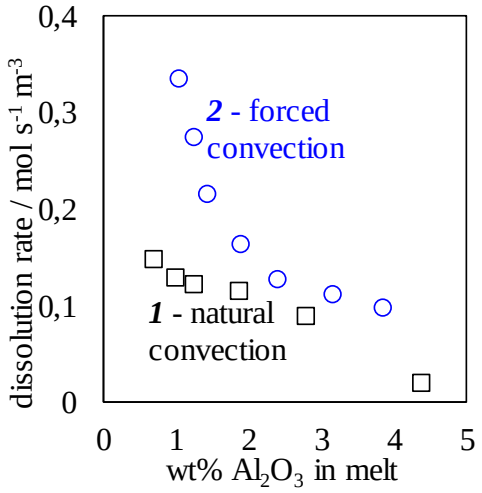

Figure 5. The effect of the alumina content in the NaF-AlF_3-CaF_2 melt ([NaF]/[AlF_3] = 2.1 mol /mol) at 970 °C on its dissolution rate.

As it was mentioned above, the electrochemical sensor of the proposed design can be used for operational monitoring the cryolite-alumina melt during electrolysis. The approbation of the sensor operation was tested on the example of electrolysis in the NaF-AlF_3-CaF_2 melt ([NaF]/[AlF_3] = 2.1 mol /mol) at 970 °C in lab electrolyzer. During electrolysis, the alumina was periodically loaded into the melt at a speed selected in accordance with the current and current efficiency.

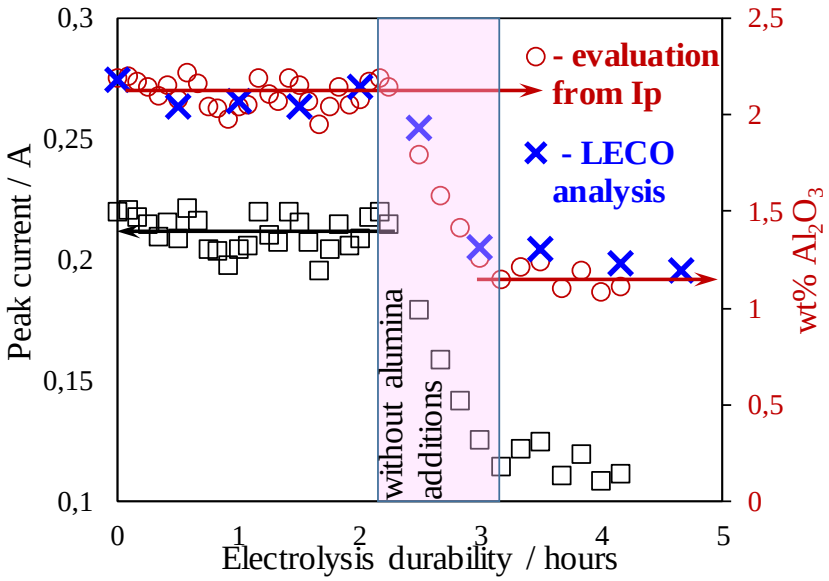

Figure 6. The dependence of the peak value of the current response on the alumina content in the NaF-AlF_3-CaF_2 melt ([NaF]/[AlF_3] = 2.1 mol /mol) at 970 °C.

The sensor readings (peak values of the current response) and the alumina content in the melt calculated according to them during electrolysis are presented in Figure6. Analytically determined values of the alumina content in the melt samples are also given. It is seen that the selected alumina feeding rate ensures a relatively stable alumina content in the melt and the sensor readings correspond to the LECO data.

Based on the preliminary results described in this work, it can be considered that the electrochemical sensor of the new optimized design is suitable both for studying the dissolution process and for monitoring the alumina content in the cryolite-alumina melt directly during electrolysis in order to optimize and increase the efficiency of aluminum electrolysis.

Conclusions

Novel electrochemical sensor (device) for monitoring the alumina content in the cryolite-alumina melt, composed of carbon working electrode and copper (or another metal interacting with aluminum) counter electrode was proposed.

The process of alumina dissolution in the cryolite-alumina melt of the conventional composition NaF-AlF_3-(5 wt%)CaF_2-Al_2O_3 ([NaF]/[AlF_3] = 2.1 mol/mol) at 970 °C was studied using the developed sensor. In particular, the rate of alumina dissolution was estimated depending on its content in the melt and convection conditions. The integral rate of the alumina dissolution was up to 0.36 mol/s·m^3.

It was found that under the selected measurement conditions the peak values of the current response recorded by the sensor linearly depend on the alumina content in the melt. The obtained empirical dependence was used for operational measurement of the alumina content during electrolysis in the cryolite-alumina melt.

Acknowledgments

This work was financially supported by the Ministry of Education and Science of the Russian Federation (Agreement No. EB 075-15-2019-1949, ext. No. 05.604.21.0239, IN RFMEFI60419X0239).

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